Chemistry of Heterocyclic Compounds, Vol. 38, No. 2, 2002

PHOTOCHROMIC DIHETARYLETHENES. 12.* SYNTHESIS OF 5-ALKYL-2-(1,3,4-OXADIAZOL-2-YL)THIOPHENES AND THEIR PHOTOCHROMIC DERIVATIVES*[2]

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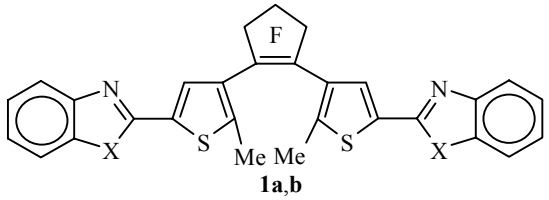
Photochromic derivatives of 5-alkyl-2-(1,3,4-oxadiazol-2-yl)thiophenes have been synthesized for the first time. Their photochromic and fluorescent properties have been studied.

Keywords: benzothiazoles, 1,2-dithienylethenes, 1,3,4-oxadiazoles, perfluorocyclopentene, photochromes, nondestructive readout of optical information, fluorescence.

One of the conditions determining the practical value of photochromic compounds is the possibility of reading optical information without destroying it. A promising approach is the method of readout using the fluorescence inherent in the actual photochrome molecule excited in the region in which a mutual transition of two forms does not occur. Today there are only a few similar examples [2,3], however no special studies directed towards obtaining fluorescing photochromic dihetarylethenes have been carried out. The development of methods for synthesis of thermally irreversible compounds capable of effecting multiple readout of information is a promising direction in the design of new photochromic structures.

Previously we obtained photochromic dihetarylethenes of general formula **1** [4,5]. Compounds **1a,b** are photochromes, but do not fluoresce. Consequently in the next step we paid attention to structures known to contain fluorescent fragments.



1a,**b**

1 a X = O, **b** X = S

* For Part 11 see [1].

*[2] Dedicated to M. G. Voronkov on the occasion of his Jubilee.

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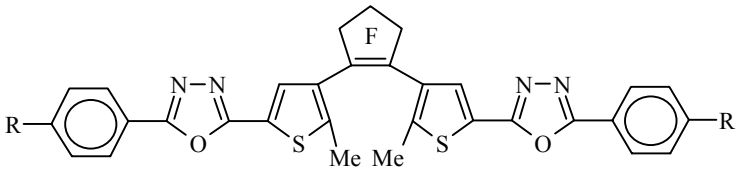
It is known that 2,5-diaryl-1,3,4-oxadiazoles are efficient organic luminophores [6]. For example, on investigating the spectral properties of 2-(2-thienyl)-5-aryl-1,3,4-oxadiazoles it was discovered that they possess a very intense fluorescence [7]. It was expedient therefore to build the photochromic system **2** containing thiophene, 1,3,4-oxadiazole, and benzene rings. In addition this combination should be capable of increasing the length of the conjugation chain. It was also interesting to consider the effect of additional functional groups in this system on the photochromic properties of the compounds.

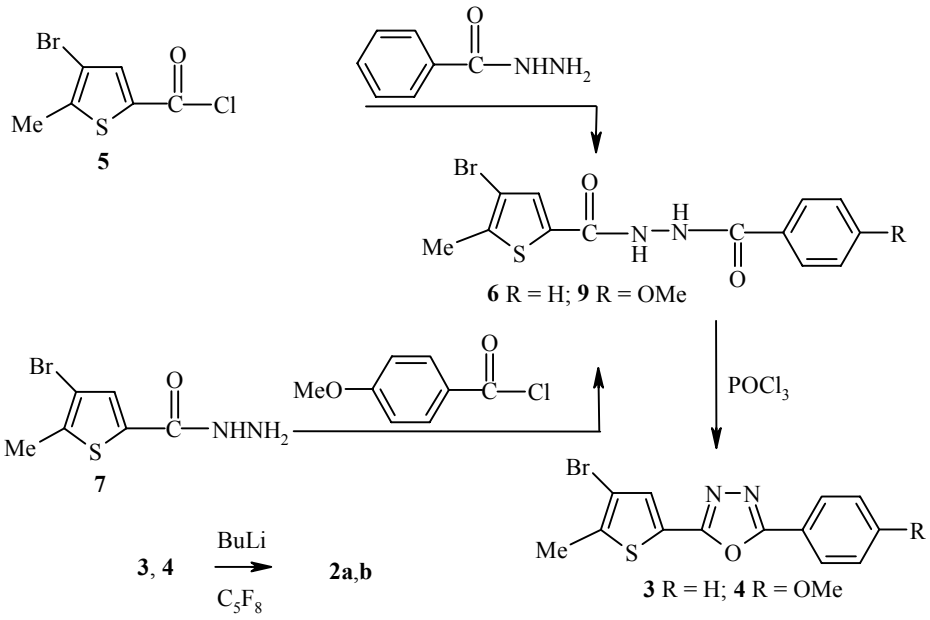


2a,**b**

2 a R = H, **b** R = OMe

The synthesis of the initial bromides **3** and **4** for the corresponding photochromic compounds **2a,b** is shown in Scheme 1. By reacting acid chloride **5** and benzoic acid hydrazide in pyridine at 60°C the diacylhydrazide **6** was obtained, which after boiling in phosphorus oxychloride for 10 h was converted in 98% yield into bromide **3**. 4-Methoxybenzoyl chloride and hydrazide **7**, obtained from methyl ester of 4-bromo-5-methyl-2-thiophenecarboxylic acid (**8**) by boiling in alcohol with an aqueous solution of hydrazine hydrate, were used for the synthesis of bromide **4**. The resulting hydrazide **9** was converted in 95% yield into compound **4** by boiling in phosphorus oxychloride.

Scheme 1



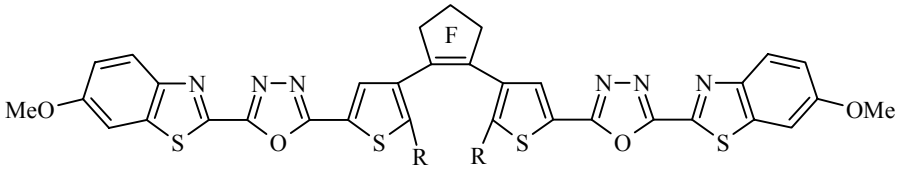
The sequential interaction of bromide **3** with BuLi and octafluorocyclopentene in THF at -70°C led to the photochromic compound **2a** in 34% yield. The structure of **2a** was established by spectral methods, and the data of elemental analysis were consistent with it. In the ^{1}H NMR spectrum singlets were observed for the methyl protons, the thiophene ring proton, and also for the benzene ring protons, which indicate the presence of one open symmetrical form. The photochromic characteristics are given in Table 1.

TABLE 1. Photochromic Characteristics of 1,2-Bis(3-thienyl)-perfluorocyclopentenes

Compound	λ_{max}, nm (ε, $M^{-1}\cdot cm^{-1}$)		Quantum yield ϕ of the photoreaction		Cyclicity
	form **A**	form **B**	**A** → **B**	**B** → **A**	
2a	311 (48700)	603 (14600)	1.0	0.014	2000
2b	318 (52700)	605 (19300)	0.85	0.01	45
10b	354 (28300)	633 (10500)	0.98	0.012	600
25	351 (38700)	570 (12900)	0.74	0.05	380

The photochromic compound **2b** was obtained analogously in 30% yield from bromide **4**. The structure of **2b** was established by spectral methods and was consistent with the data of elemental analysis. Singlets were observed in the ^{1}H NMR spectrum for the methyl protons of the OCH_3 group and for the thiophene ring proton. There were also two signals for the aromatic protons, which were doublets with J ~8 Hz.

It turned out unexpectedly that in spite of the presence of fluorophoric fragments, compounds **2a,b** did not possess fluorescent properties. We have therefore made attempts in the present work to synthesize derivatives of the photochromic system **10** containing simultaneously thiophene, 1,3,4-oxadiazole, and benzothiazole rings, which in our opinion may display fluorescent properties.



10a,**b**

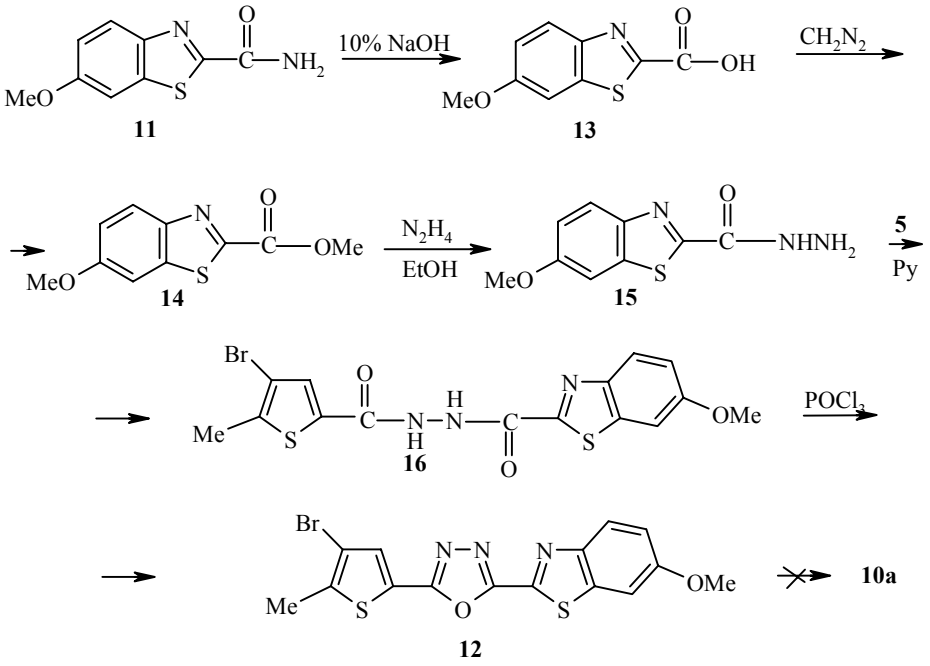
10 a R = Me, **b** R = C_6H_{13}

A convenient starting material for the synthesis of substances **10a,b** is 2-carbamoyl-6-methoxybenzothiazole (**11**), a method of obtaining which was recently developed by us [8]. Amide **11** is also interesting as it serves as a starting material for the synthesis of *D*(-)-2-(6-hydroxy-2-benzothiazolyl)-3,4-dihydrothiazole-4-carboxylic acid (luciferin), the substance providing the glow of fireflies [9], and widely used for some time in biophysical investigations. Starting from benzothiazole **11**, the synthesis of 2-(4-bromo-5-methyl-2-thienyl)-5-(6-methoxy-2-benzothiazolyl)-1,3,4-oxadiazole (**12**) was effected as in Scheme 2.

6-Methoxybenzothiazole-2-carboxylic acid (**13**), obtained on saponification of amide **11** in 10% aqueous NaOH solution, was converted into the corresponding methyl ester **14,** which gives hydrazide **15** after boiling in alcohol with an aqueous solution of hydrazine hydrate. Interaction of compound **15** with 4-bromo-5-methyl-2-thienoyl chloride (**5**) leads to the diacylhydrazine **16**. Its cyclization to oxadiazole **12** under the action of phosphorus oxychloride at atmospheric pressure did not proceed to completion. Even on extended boiling the ratio of starting material to reaction product was 10:3. After heating in an ampul for 20 h at 140°C the yield of bromide **12** was 40% and at 160-170°C for 16 h the yield was successfully increased to 70%.

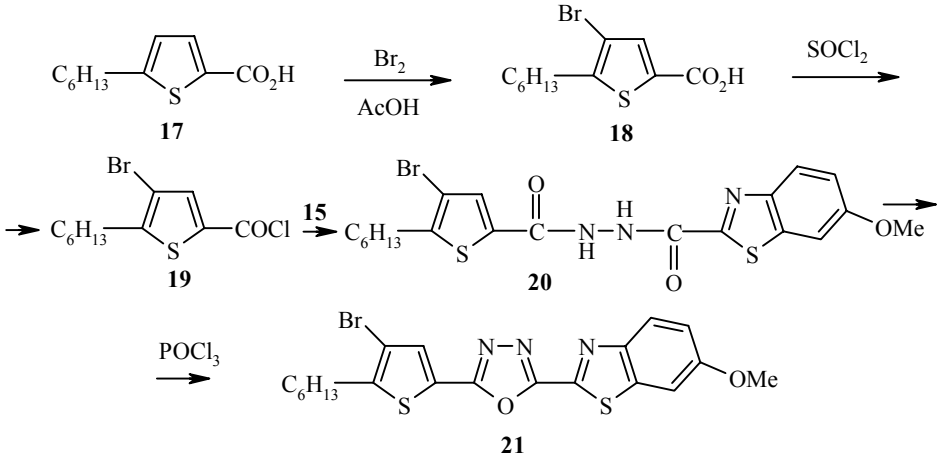
Regretably, our numerous attempts to obtain the photochromic compound **10a** from bromide **12** were unsuccessful due to its poor solubility in THF, and in mixtures of THF–toluene, THF–HMPA at -70°C. Starting material was recovered in 30-50% yield, the remainder (70-50%) were resinous products. It should be mentioned that an increase in the reaction time of bromide **12** with BuLi led to darkening of the reaction mixture and to an increase in the formation of resinification products.

Scheme 2



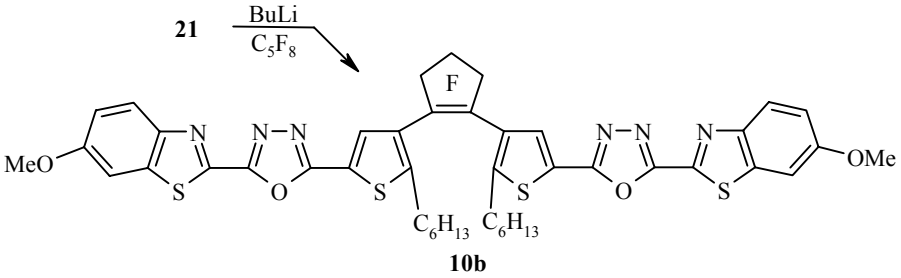
To increase the solubility of the initial bromide it was decided to replace the methyl residue in position 2 of the thiophene ring by hexyl (Scheme 3). 4-Bromo-5-hexylthiophene-2-carboxylic acid (**18**) was obtained for this purpose by the bromination of 5-hexylthiophene-2-carboxylic acid (**17**) in acetic acid in the presence of $FeCl_3$. Interaction of its acid chloride **19** with hydrazide **15** and subsequent cyclization of the diacyl hydrazine **20** under the same conditions as for compound **16** gave product **21**.

Scheme 3



On sequential interaction of bromide **21** with BuLi and C_5F_8 the photochromic compound **10b** was synthesized (Scheme 4) in low yield (2%) and was characterized by ^{1}H NMR and mass spectrometry. In the ^{1}H NMR spectrum a singlet and two doublets (J ~8 Hz) were observed for the protons of the benzothiazole fragment, a singlet for the thiophene ring proton, and signals for the protons of the hexyl group.

Scheme 4

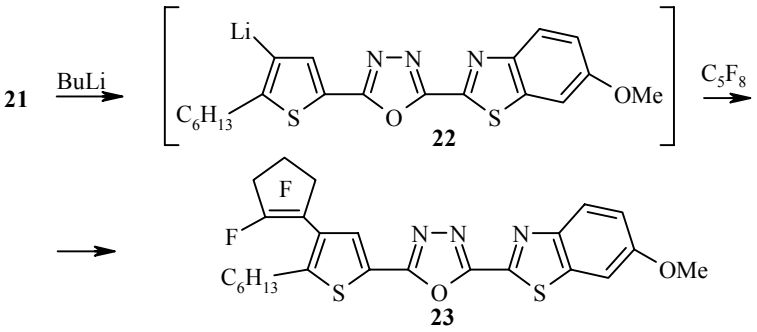


10b

On photochemical investigation of compound **10b** it was discovered that its open form possesses fluorescence (Table 1).

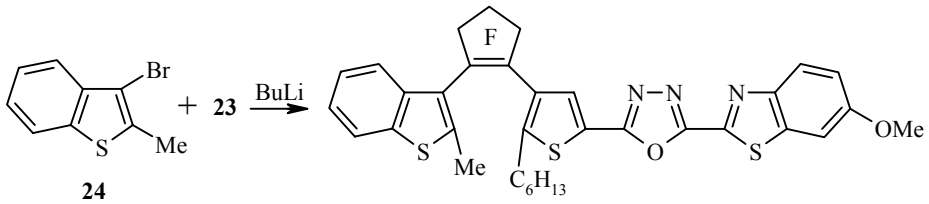
By the action of an excess of octafluorocyclopentene on the Li derivative **22**, obtained from bromide **21,** we synthesized (Scheme 5) the mono derivative **23** in 9% yield and characterized it by ^{1}H NMR and mass spectrometry.

Scheme 5



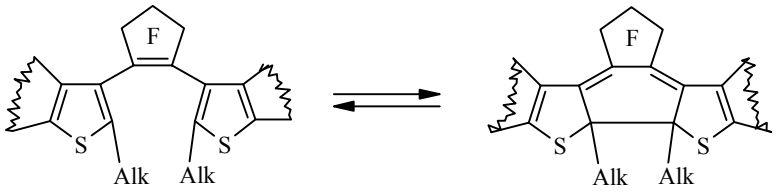
The unsymmetrical compound **25** was synthesized in 29% yield by the reaction of fluoride **23** with 3-bromo-2-methylbenzothiophene (**24**) (Scheme 6). The structure of product **25** was established by data of elemental analysis and by spectral methods. Signals were observed in the ^{1}H NMR spectrum for the protons of the benzothiazole fragment, viz. a singlet and two doublets (J ~8 Hz), a singlet for the proton of the thiophene ring, signals for the protons of the benzothiophene fragment, and also signals for the protons of the methyl, hexyl, and methoxy groups.

Scheme 6



It was discovered in the photochemical investigation of compound **25** that its open form possesses fluorescence (Table 1).

A photochemical study of compounds **2a**,**b**, **10b**, and **25** was carried out in acetonitrile. Photocyclization of **A**→ **B** was effected on irradiating with light of λ 313 and 365 nm, and the reverse reaction **B** → **A** on irradiating with light of λ 578 nm.



A **B**

Isosbestic points were observed in the absorption spectra. The coincidence of their position on carrying out the forward and reverse reactions indicate the complete reversibility of photocyclization and the absence of side processes (see Figs. 1, 2).

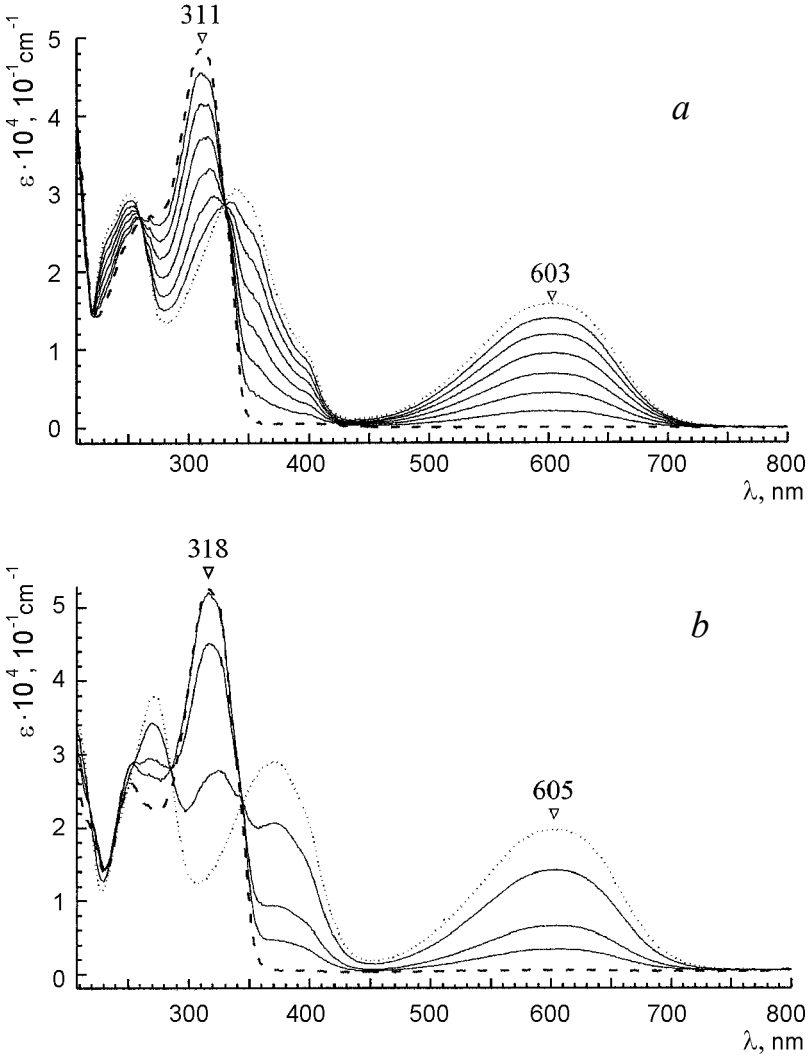


Fig.1. Change in absorption spectrum for acetonitrile solutions of *a*) compound **2a** and *b*) compound **2b** on irradiating with light of λ 313 (forward reaction) and 578 nm (reverse reaction).

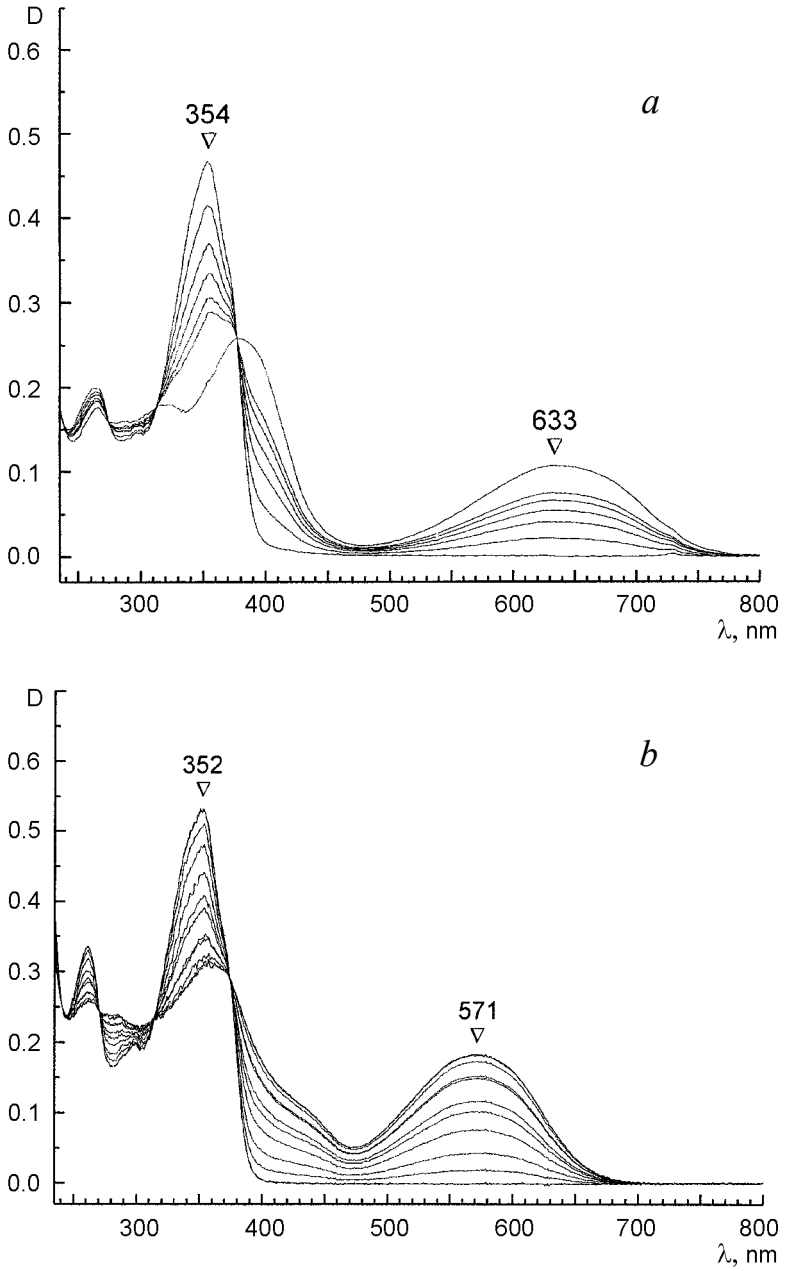


Fig. 2. Change in absorption spectrum for acetonitrile solutions of *a*) compound **10b** and *b*) compound **25** on irradiating with light of λ 365 (forward reaction) and 578 nm (reverse reaction).

The differences in the positions of the long wave absorption bands of compounds **2a** and **2b** were insignificant. The large bathochromic shift of the long wave absorption bands of **10bB** relative to **25B** is caused primarily by the significant lengthening of the conjugation chain (the cyclic forms of the photochromes with benzothienyl substituents on the perfluorocyclopentene ring absorb in a shorter wave region than their analogs with alkyl- and aryl-substituted thienyl fragments [10]), and secondly by the presence of a second *n*-hexyl substituent in place of methyl at position 2 of the thiophene ring. The dark ring fission reaction (**B** → **A**) was absent for **2a**, **2b** and **25**, and the cyclic form **10bB** was thermally unstable. After 100 h exposure in the dark the optical density of this form was reduced by 2% (after 530 h by 15%).

Compounds **2a** and **2b** did not fluoresce. The open forms **25A** and **10bA** fluoresce, the intensity of the fluorescence fell sharply after cyclization under the action of UV light with λ 365 nm. The fluorescence emission maximum of **25A** was at λ 428 nm and of **10bA** at λ 422 nm. The fluorescence excitation spectrum, repeating the absorption spectrum, indicates that the observed fluorescence belongs to the fluorescence of **10bA**.

The presence of fluorophoric fragments in the structures of photochromic dithienylethenes does not by any means always lead to the development of fluorescence by the latter, and the presence of fluorescence in **25A** and **10bA** is probably explained by the adequate separation of the benzothiazole substituent from the perfluorocyclopentene fragment directly involved in the photochromic conversion.

EXPERIMENTAL

The ^{1}H, ^{13}C, and ^{19}F NMR spectra were taken on Bruker WM 200 (200 MHz) and AM 300 (300 MHz) spectrometers for solutions in $CDCl_3$, $(CD_3)_2CO$, or $(CD_3)_2SO$. Mass spectra were obtained on a Finnigan MAT INCOS 50 (70 eV) instrument in chromatography mode (capillary column RSL 200 of length 30 m) or by direct insertion. The composition of reaction mixtures was checked by ^{1}H NMR and thin-layer chromatography (TLC) on Silufol plates in systems of various polarity. Preparative separation was carried out by column chromatography on silica gel L 40-100 mesh with eluents of various polarity.

All reactions with organolithium compounds were carried out in a dry argon atmosphere. Reactants and solvents were dried using standard procedures. Reactants were introduced into previously dried apparatus using rubber stoppers and disposable syringes. Melting points were determined on a Boetius stage. The elemental analysis of compounds obtained was carried out in the Microanalysis Laboratory of the Institute of Organic Chemistry of the Russian Academy of Sciences. The irradiation of samples in the photochemical investigations was carried out with a DRSh-500 high pressure mercury lamp. The radiation intensity of the mercury lamp was determined with an F4 photocell calibrated with a ferrioxalate actinometer [11] for λ 313, 365, 405, and 436 nm and an actinometer based on Reinecke salt [12] for λ 546 and 578 nm. Absorption spectra were recorded on a Shimadzu UV 2101PC spectrophotometer. Fluorescence was investigated with the aid of a Perkin–Elmer LS 50 spectrofluorimeter. To determine quantum yield a solution of the substance in ethanol was irradiated with light at λ 365 nm when carrying out photocyclization and at 578 nm for the reverse reaction using light filters to separate the lines of the mercury spectrum. The duration of irradiation was gradually increased from 5 sec to 1-2 min (7-10 experimental points in all), the absorption spectrum of the irradiated solution was recorded for each exposure.

To determine cyclicity an undegassified solution of the photochrome was subjected to irradiation over a wide range, including the lines of the mercury spectrum at 313, 365, 405, 436, 546, and 578 nm. The ratio of the intensities of the lines in the mercury spectrum in the UV and visible regions was varied using wide-band filters. The time of irradiation during which one photocycle was effected was determined from the formula:

$$\tau = \frac{c_0 \phi_{\mathbf{B}\rightarrow\mathbf{A}}}{J_a^{\mathbf{B}}}$$

where c_0 is the initial concentration of substance, $\phi_{\mathbf{B}\rightarrow\mathbf{A}}$ the quantum yield for the conversion of **B** to **A**, $J_a^{\mathbf{B}}$ is the intensity of light absorbed by form **B** in the photostationary state.

4-Bromo-5-methylthiophene-2-carboxylic Acid Chloride (5). Thionyl chloride (6 ml, 0.08 mol) was added to 4-bromo-5-methylthiophene-2-carboxylic acid [13] (7 g, 0.03 mol) and the mixture was boiled under reflux for 2 h. The solution was then cooled to room temperature and left overnight. Unreacted $SOCl_2$ was removed, the residue distilled in vacuum, collecting the fraction with bp 137-138°C, P = 15 torr. Yield of **5** 78%; mp 32.5-34.5°C.

1-(4-Bromo-5-methyl-2-thienoyl)-2-benzoylhydrazine (6). Acid chloride **5** (2.48 g, 0.01 mol) was added to a stirred solution of benzoic acid hydrazide (1.36 g, 0.01 mol) in pyridine (10 ml) at 10°C. The mixture was stirred at room temperature for 20 min, then heated for 2 h at 60°C. The reaction mixture was brought to room temperature and left overnight. The mixture was poured into water (50 ml), the precipitated solid filtered off, washed with water, and dried. Ethanol (100 ml) was added to the substance obtained, the mixture heated under reflux for 1 h, the solid was then filtered off, and dried. Yield 61%; mp 286-288°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.45 (3H, s, CH_3); 7.52 (2H, m, H arom.); 7.60 (1H, m, H arom.); 7.81 (1H, s, H thiophene); 7.91 (2H, m, H arom.); 10.48 (2H, *cis*-s, NH). Mass spectrum, *m/z* (I_{rel}, %): 340 $[M]^+$ (44%).

4-Bromo-5-methyl-2-(5-phenyl-1,3,4-oxadiazol-2-yl)thiophene (3). Phosphorus oxychloride (20 ml) was added to diacylhydrazine **6** (1 g, 2.9 mmol) and the mixture boiled under reflux for 10 h. The unreacted phosphorus oxychloride was removed, the residue was washed on the filter with water, and dried. Yield 98%; mp 168.5-169.5°C (EtOH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.46 (3H, s, CH_3); 7.60 (1H, br d, *p*-H); 7.65 (2H, br t, *m*-H); 7.87 (1H, s, H thiophene); 8.07 (2H, br d, *o*-H). Mass spectrum, *m/z* (I_{rel}, %): 320 $[M]^+$ (38%). Found, %: C 48.36; H 2.84; Br 24.38; S 9.78. $C_{13}H_9BrN_2OS$. Calculated, %: C 48.61; H 2.82; Br 24.88; S 9.98.

4-Bromo-5-methylthiophene-2-carboxylic Acid Hydrazide (7). An aqueous solution (3 ml) of $N_2H_4.H_2O$ (3 ml) was added to a solution of 4-bromo-5-methylthiophene-2-carboxylic acid methyl ester (1.3 g, 5.5 mmol) in methanol (5 ml) and the mixture boiled under reflux for 2.5 h. The precipitated solid was filtered off, washed with water, and with alcohol. Yield 90%; mp 167-168°C (EtOH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.39 (3H, s, CH_3); 4.5 (2H, s, NH_2); 7.61 (1H, s, H thiophene); 9.76 (1H, s, NH). Found, %: C 30.93; H 2.92; Br 34.17; S 13.71. $C_6H_7BrN_2OS$. Calculated, %: C 30.65; H 3.0; Br 33.99; S 13.64.

1-(4-Bromo-5-methyl-2-thienoyl)-2-(4-methoxybenzoyl)hydrazine (9) was obtained analogously to diacylhydrazine **6** from hydrazide **7** (1.5 g, 6.4 mmol) and 4-methoxybenzoyl chloride (1.1 g, 6.5 mmol). Yield 95%; mp 264-265°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.45 (3H, s, CH_3); 3.85 (3H, s, OCH_3); 7.08 (2H, d, H arom.); 7.81 (1H, s, H thiophene); 7.9 (2H, d, H arom.); 10.95 (2H, s, NH).

2-(4-Bromo-5-methyl-2-thienyl)-5-(4-methoxyphenyl)-1,3,4-oxadiazole (4) was obtained analogously to compound **3** from diacylhydrazine **9**. Yield 70%; mp 167-168°C (EtOH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.49 (3H, s, CH_3); 3.88 (3H, s, OCH_3); 7.16 (2H, d, H arom.); 7.81 (1H, s, H thiophene); 8.01 (2H, d, H arom.). Found, %: C 47.56; H 2.98; Br 22.51; S 8.90. $C_{14}H_{11}BrN_2O_2S$. Calculated, %: C 47.88; H 3.16; Br 22.75; S 9.13.

1,2-Bis[2-methyl-5-(5-phenyl-1,3,4-oxadiazol-2-yl)-3-thienyl]hexafluorocyclopentene (2a). A solution of BuLi (0.9 ml, 1.78 mmol) in hexane was added to a stirred suspension of compound **3** (0.5 g, 1.56 mmol) in abs. THF (10 ml) at -70°C in an atmosphere of Ar, and the mixture stirred at this temperature for 15 min. Octafluorocyclopentene (0.16 g, 0.78 mmol) in abs. THF (1 ml) was then added at -70°C and the mixture stirred for 2 h. The temperature of the reaction mixture was brought up to room temperature and the mixture left overnight in an atmosphere of Ar. The mixture was cooled to -5°C, alcohol (5 ml) was added, and the mixture stirred at 20°C for 40 min. The solvent was removed, the residue dissolved in $CHCl_3$, the solution washed with 5% $NaHCO_3$, with water, and dried over $CaCl_2$. The solvent was removed. The product was separated on a column of silica gel (eluent $CHCl_3$). Yield 34%; mp 236-238°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.09 (3H, s, CH_3); 7.50-7.51 (3H, m, H arom.); 7.81 (1H, s, H thiophene); 8.14 (2H, m, H arom.). Mass spectrum, *m/z* (I_{rel}, %): 656 $[M]^+$ (10%). Found, %: C 56.45; H 2.58. $C_{31}H_{18}F_6N_4O_2S_2$. Calculated, %: C 56.71; H 2.76.

1,2-Bis{2-methyl-5-[5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-yl]-3-thienyl}hexafluorocyclopentene (2b) was obtained analogously to **2a** from bromide **4**. The product was isolated by column chromatography (eluent hexane–ethyl acetate from 10:1 to 3:1). Yield 30%; mp 219-220.5°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.19 (3H, s, CH_3); 3.89 (3H, s, OCH_3); 7.01 (2H, d, H arom.); 7.75 (1H, s, H thiophene); 8.02 (2H, d, H arom.). Found, %: C 56.04; H 3.13; S 9.05. $C_{33}H_{22}F_6N_4O_4S_2$. Calculated, %: C 55.31; H 3.09; S 8.95.

6-Methoxybenzothiazole-2-carboxylic Acid (13). A 10% NaOH solution (75 ml) was added to amide **11** (3 g, 14 mmol) and the mixture was boiled under reflux for 45 min. The suspension was cooled, the solid

filtered off, washed with benzene, dried, dissolved in water (400 ml), and the solution acidified with conc. HCl. The precipitated solid was filtered off, washed with water, and dried. Yield 80%; mp 106°C (105-108°C in [9]).

6-Methoxybenzothiazole-2-carboxylic Acid Methyl Ester (14). An ether solution of CH_2N_2 (1 g, 24 mmol) was added during 15 min to a stirred solution of acid **13** (2 g, 9.56 mmol) in THF (50 ml) at 1°C. The temperature of the reaction mixture was brought to room temperature, and the mixture stirred for 2 h. The solvent was removed, and the residue crystallized from methanol. Yield of ester **14** was 66%; mp 142-143°C (MeOH) (142-142.8°C in [9]).

6-Methoxybenzothiazole-2-carboxylic Acid Hydrazide (15). An aqueous solution (2 ml) of $N_2H_4 \cdot H_2O$ was added to a solution of ester **14** (1.3 g, 5.8 mmol) in methanol (20 ml) and the mixture boiled under reflux for 2.5 h. The precipitated solid was filtered off, washed with water, and then with alcohol. Yield 87%; mp 223-225°C (EtOH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.88 (3H, s, OCH_3); 4.7 (2H, br. s, NH_2); 7.21 (1H, d, H arom.); 7.78 (1H, s, H arom.); 8.0 (1H, d, H arom.); 10.3 (1H, br. s, NH). Found, %: C 48.29; H 3.78; S 13.89. $C_9H_9N_3O_2S$. Calculated, %: C 48.42; H 4.06; S 14.36.

1-(4-Bromo-5-methyl-2-thienoyl)-2-(6-methoxy-2-benzothiazolyl)hydrazine (16) was obtained analogously to diacylhydrazine **6** from hydrazide **15** and acid chloride **5**. Yield 78%; mp 259-260°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.47 (3H, s, CH_3); 3.90 (3H, s, OCH_3); 7.19 (1H, d, H arom.); 7.70 (1H, s, H thiophene); 7.8 (1H, s, H arom.); 8.2 (1H, d, H arom.); 10.61 (1H, s, NH); 10.9 (1H, br. s, NH).

2-(4-Bromo-5-methyl-2-thienyl)-5-(6-methoxy-2-benzothiazolyl)-1,3,4-oxadiazole (12). A solution of compound **16** (1 g, 2.3 mmol) in $POCl_3$ (17 ml) was heated for 16 h in an ampul at 160-170°C. The phosphorus oxychloride was removed, the residue washed on the filter with water, and dried. Yield 70%; mp 277-278°C (Py). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.52 (3H, s); 3.96 (3H, s, OCH_3); 7.21 (1H, d, H arom.); 7.41 (1H, s, H arom.); 7.79 (1H, s, H thiophene); 8.11 (1H, d, H arom.). Mass spectrum, *m/z* (I_{rel}, %): 407 $[M]^+$ (100). Found, %: C 43.85; H 2.35; Br 19.32; S 15.35. $C_{15}H_{10}BrN_3O_2S_2$. Calculated, %: C 44.13; H 2.47; Br 19.57; S 15.70.

5-Hexylthiophene-2-carboxylic Acid (17). An ether solution of BuLi (66 ml, 97 mmol) was added to a stirred solution of 2-hexylthiophene [14] (15 g, 89 mmol) in ether (150 ml) at room temperature in an atmosphere of Ar. The mixture was stirred for 0.5 h at room temperature, boiled for 1 h under reflux, and stirred for 1 h at 20°C. The solution was poured into a mixture of dry ice (200 g) and ether (500 ml). After 2 h water (200 ml) was added, the layers were separated, the organic layer was washed with 5% NaOH solution. The combined aqueous fraction was acidified with conc. HCl. The precipitated solid was filtered off, and washed with water. Yield 87%; mp 60-62°C (65°C in [15]).

4-Bromo-5-hexylthiophene-2-carboxylic Acid (18). A solution of bromine (7.5 g, 47 mmol) in acetic acid (9 ml) was added during 1.5 h to a stirred solution of acid **17** (10 g, 47 mmol) in acetic acid (100 ml) at room temperature in the presence of $FeCl_3$ (1.3 g, 8 mmol). The mixture was stirred for 2 h, boiled under reflux for 6 h, then cooled to room temperature. The mixture was poured into water (1 liter), the precipitated solid was filtered off, washed with water, and dried. Yield 65%, mp 86-86.5°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.85-0.99 (3H, m); 1.38-1.49 (6H, m); 1.66-1.78 (2H, m); 2.85 (2H, t); 7.71 (1H, s, H thiophene). Found, %: C 45.19; H 4.95. $C_{11}H_{15}BrO_2S$. Calculated, %: C 45.37; H 5.19.

4-Bromo-5-hexyl-2-thienoyl Chloride (19) was obtained analogously to acid chloride **5** from acid **18**. After removing the $SOCl_2$ in vacuum the acid chloride **19** was used without further purification.

1-(4-Bromo-5-hexyl-2-thienoyl)-2-(6-methoxy-2-benzothiazolyl)hydrazine (20) was obtained analogously to diacylhydrazine **6** from hydrazide **15**. Yield 98%; mp 153-156°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.9 (3H, s, CH_3); 1.32-1.65 (8H, m, CH_2); 2.79 (2H, t, CH_2); 3.9 (3H, s, OCH_3); 7.17 (1H, d, H arom.); 7.38 (1H, s, H thiophene); 7.56 (1H, s, H arom.); 7.96 (1H, d, H arom.); 9.39 (1H, br. s, NH); 9.84 (1H, br. s, NH). Mass spectrum, *m/z* (I_{rel}, %): 495 $[M]^+$ (6).

2-(4-Bromo-5-hexyl-2-thienyl)-5-(6-methoxy-2-benzothiazolyl)-1,3,4-oxadiazole (21) was obtained analogously to compound **12** from diacylhydrazine **20**. Yield 60%; mp 157.5-158°C (AcOEt). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.91 (3H, t); 1.31-1.45 (6H, m); 1.65-1.79 (2H, m); 2.85 (2H, t); 3.92 (3H, s, OCH_3);

7.19 (1H, d, H arom.); 7.41 (1H, s, H arom.); 7.79 (1H, s, H thiophene); 8.10 (1H, d, H arom.). Mass spectrum, *m/z* (I_{rel}, %): 477 $[M]^+$ (55). Found, %: C 49.91; H 4.0; Br 16.38; S 13.21. $C_{20}H_{20}BrN_3O_2S_2$. Calculated, %: C 50.20; H 4.21; Br 16.70; S 13.40.

1,2-Bis{2-hexyl-5-[5-(6-methoxy-2-benzothiazolyl)-1,3,4-oxadiazol-2-yl]-3-thienyl}perfluorocyclopentene (10b) was obtained analogously to product **2a** from bromide **21** and was isolated (6 mg, 2%) on a chromatographic column (eluent benzene–$CHCl_3$, 1:1). Mp 203-204°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.75-0.95 (3H, m); 1.1-1.45 (8H, m); 2.35 (2H, t); 3.95 (3H, s, OCH_3); 7.29 (1H, d, H arom.); 7.45 (1H, s, H arom.); 7.96 (1H, s, H thiophene); 8.14 (1H, d, H arom.). Mass spectrum, *m/z* (I_{rel}, %): 970 $[M]^+$ (10).

1-{2-Hexyl-5-[5-(6-methoxy-2-benzothiazolyl)-1,3,4-oxadiazol-2-yl]-3-thienyl}heptafluorocyclopentene (23). A solution (2.1 ml, 3.0 mmol) of BuLi in hexane was added to a stirred solution of bromide **21** (1.3 g, 2.7 mmol) in abs. THF (30 ml) at -70°C in an atmosphere of Ar. Stirring was continued at the same temperature for 15 min, then octafluorocyclopentene (0.7 ml, 5.4 mmol) was added at -70°C and the mixture stirred for 2 h. The reaction mixture was brought to room temperature and left overnight. The mixture was cooled to -5°C, alcohol (5 ml) was added, and the mixture stirred for 40 min at 20°C. The solvent was removed, the residue was washed on the filter with water, and dried. The product was separated on a chromatographic column (eluent ether–hexane, 1:1). Yield 9%; mp 136-138°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.86-0.97 (3H, m); 1.3-1.43 (6H, m); 1.7-1.8 (2H, m); 2.85 (2H, t); 3.95 (3H, s, OCH_3); 7.21 (1H, d, H arom.); 7.42 (1H, s, H arom.); 7.88 (1H, s, H thiophene); 8.11 (1H, d, H arom.). Mass spectrum, *m/z* (I_{rel}, %): 591 $[M]^+$ (100).

1-{2-Hexyl-5-[5-(6-methoxy-2-benzothiazolyl)-1,3,4-oxadiazol-2-yl]-3-thienyl}-2-[2-methyl-3-benzothiophenyl]perfluorocyclopentene (25). A solution (0.35 ml, 0.5 mmol) of BuLi in hexane was added at -68°C in an atmosphere of Ar to a solution of compound **24** [16] (0.11 g, 0.5 mmol) in abs. THF (20 ml) and the mixture was stirred at this temperature for 15 min. Compound **23** (0.12 g, 0.2 mmol) in abs. THF (5 ml) was then added at -70°C, and the mixture stirred for 2 h at the same temperature. The reaction mixture was brought up to room temperature and left overnight in an atmosphere of Ar. The mixture was cooled to -5°C, alcohol (5 ml) was added, and the mixture stirred for 0.5 h at 20°C. The solvents were removed, water (5 ml) was added to the residue, the solid filtered off, and dried. The product was separated on a chromatographic column (eluent ethyl acetate–hexane, 1:4). Yield was 29%; mp 207-208°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.85 (3H, t); 0.9-1.36 (8H, m); 2.05-2.21 (2H, m); 2.30 (3H, s, CH_3); 3.95 (3H, s, OCH_3); 7.20 (1H, d, H arom.); 7.28 (1H, m, H arom.); 7.36 (1H, m); 7.41 (1H, s, H arom.); 7.61 (1H, m, H arom.); 7.79 (1H, d, H thiophene); 7.99 (1H, s, H arom.); 8.04 (1H, d). Mass spectrum, *m/z* (I_{rel}, %): 719 $[M]^+$ (50).

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